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# A MODEL FOR REMOVAL OF SURFACE-BOUND TRITIUM USING HUMID AIR

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*A model has been developed to describe the observed release rate of tritium from a research-scale laser inertial confinement fusion chamber during humid air purge cycles. The relative roles of successive rate limiting processes active during the purge cleaning process are assessed and incorporated into a system-level description that includes the coupled effects of convection, surface reaction, and sub-surface diffusion on tritium removal rate. The computational effort required for solution of the model equations is modest owing to the dominant roles of surface reaction and bulk diffusion, both of which may be adequately treated using low-dimension approximations. The resulting formalism is sufficiently general to be applied to a wide range of systems, materials, and process conditions involving water-gas interaction with tritium bearing surfaces.*

## I. INTRODUCTION

The ability of humid air to remove tritium surface contamination is well known in the tritium processing and research community<sup>1</sup>. The role of water in the promotion of tritium release from contaminated surfaces is generally understood not only in terms of its adsorption and desorption characteristics, but also its chemical reaction potential for exchange of protons with surface tritons in similarly bound states<sup>2</sup>. A further common observation regarding the rate of tritium release from many contaminated materials is that at some point in the tritium release process, the measured gas phase tritium concentration decreases in proportion to  $1/\sqrt{t}$ , indicating bulk diffusion as the rate-limiting process. With these general mechanisms in mind, we have reviewed effluent data taken during humid air purging of the Omega target chamber at the University of Rochester's Laboratory for Laser Energetics following a series of ICF experiments where a total of 6 mols (6.44 GBq) of tritium were released into the process chamber during an extended campaign of DT target shots<sup>3</sup>. We find analysis of the effluent stream tritium concentration history provides considerable insight into the underlying rate processes governing the observed tritium release over time.

## II. THEORY AND MODEL EQUATIONS

The physical picture for removal of tritium from a surface using humid air is shown by Figure 1. Using a well-mixed approximation for convection in the chamber

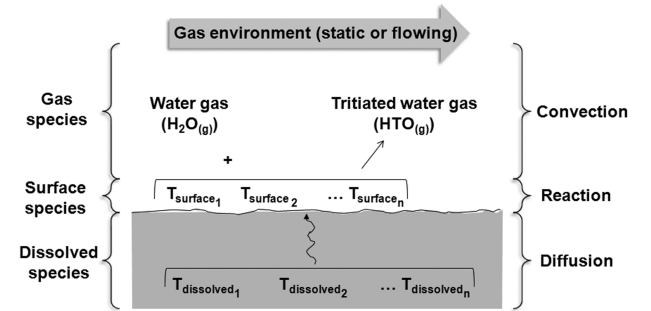


Fig.1 Physical picture for humid air cleaning of tritiated surfaces.

we write for the mass balance of gas-phase tritium (as HTO)

$$V_{ch} \frac{dp_{HTO}}{dt} = k'_G (\theta_{HTO}^* - \theta_{HTO}) + Q_{purge} p_{HTO} \quad (1)$$

where  $V_{ch}$  is the chamber volume,  $p_{HTO}$  is the partial pressure of HTO,  $k'_G$  is a convection mass transfer coefficient expressed in units appropriate for a driving force based on surface coverage,  $\theta_{HTO}^*$  is the fractional surface coverage of HTO in equilibrium with  $p_{HTO}$ ,  $\theta_{HTO}$  is the actual fractional coverage of HTO on the chamber walls, and  $Q_{purge}$  is the total volumetric flow rate of purge gas. In general, the equilibrium surface coverage of water isotopologues will be a function of corresponding concentrations in the adjacent gas phase. We therefore express the HTO equilibrium surface coverage  $\theta_{HTO}^*$  as

$$\theta_{HTO}^* = \frac{p_{HTO}}{p_{HTO} + p_{H_2O}} f(p_{HTO} + p_{H_2O}) \quad (2)$$

where the functional relation must be determined by experiment or theory for the particular material(s) under

consideration. In this work we have for convenience used an experimentally determined water isotherm for aluminum oxide<sup>4</sup> in (2) however, because  $p_{H_2O}$  in the purge stream was held constant at approximately 950 Pa (40% RH), other than setting the nominal water surface concentration at approximately 2.5 monolayers<sup>4</sup>, the precise functional form of the isotherm plays a negligible role in the analysis of this particular data.

Evolution of detector HTO partial pressure  $p_{HTO\_det}$  is also obtained by mass balance as

$$V_{det} \frac{dp_{HTO\_det}}{dt} = Q_{purge} (p_{HTO} - p_{HTO\_det}). \quad (3)$$

The evolution of surface adsorbed HTO coverage  $\theta_{HTO}$  in the chamber is determined by the balance between surface reaction and convection transport into the gas phase according to

$$\begin{aligned} \frac{d\theta_{HTO}}{dt} = & -k_r \theta_{OH} p_{HTO} + k_f \theta_{OT} p_{H_2O} \\ & - k_G'' (\theta_{HTO}^* - \theta_{HTO}), \end{aligned} \quad (4)$$

where  $k_r$  and  $k_f$  are reverse and forward reaction rate constants for the isotope exchange reaction



and  $\theta_{OH}$ ,  $\theta_{OT}$ , and  $\theta_{H_2O}$  are the surface fractions of protium and tritium hydroxyls and water. The double prime on  $k_G''$  of (4) indicates additional unit conversion factors. In this analysis we use for the isotope exchange reaction  $K_{eq}=6.0$ , the equilibrium constant for homogeneous gas phase reaction of tritium and water at room temperature<sup>5</sup>. Because the system runs with continual water supply and exhaust, the reactions remain far from equilibrium and the magnitude of the reverse reaction remains negligible. Consequently, the exact value of  $K_{eq}$  used is relatively unimportant however, inclusion of reverse reaction terms is necessary to enforce reasonable asymptotic behavior of the numerical solution.

The evolution equation for surface-bound tritium is then

$$\begin{aligned} \frac{d\theta_{OT}}{dt} = & +k_r \theta_{OH} p_{HTO} - k_f \theta_{OT} p_{H_2O} \\ & + D'_{ab} \left. \frac{dc_{T\_b}}{dx} \right|_{surface}. \end{aligned} \quad (6)$$

If multiple surface reactions are evident, (3-6), and their analogs for surface water evolution will contain multiple  $k_f/k_r$  paired terms, one set for each unique mechanism. The third right hand side term in (6) is the surface flux (defined positive for negative concentration gradients) resulting from diffusion of tritium from the bulk and is

obtained by solution of the transient 1-D diffusion equation

$$\frac{\partial c_{T\_b}}{\partial t} = \frac{\partial}{\partial x} \left\{ D_{ab} \frac{\partial c_{T\_b}}{\partial x} \right\} \quad (7)$$

with the surface boundary condition  $c_{T\_b} = s \theta_{T_{tot}}$  where  $s$  is a solubility constant for atomic tritium in the bulk immediately adjacent to the interface,  $c_{T\_b}$  is the bulk atomic tritium concentration, and  $D_{ab}$  is the bulk diffusivity of atomic tritium (the primed version  $D'_{ab}$  in (6) includes additional unit conversion factors). The total system of equations is closed by writing analogs to (1-7) involving the protiated specie concentrations  $p_{H_2O}$ ,  $p_{H_2O\_det}$ ,  $\theta_{H_2O}^*$ ,  $\theta_{H_2O}$ ,  $\theta_{OH}$ , and  $c_{H\_b}$ .

### III. HUMID AIR PURGE DATA FROM THE LLE OMEGA CHAMBER

In a 2006 report<sup>3</sup> the effluent tritium concentration history during humid air purge of the Omega ICF process chamber was given along with a description of the system configuration and process conditions. Fig.2 shows the ionization chamber data taken during the 4 hr humid air purge. Under the reported conditions the inlet and chamber Reynolds numbers were  $1.9 \times 10^4$  and  $1.9 \times 10^3$  respectively, indicating fully developed turbulent flow of the inlet jet and an average flow characteristic in the chamber of decaying turbulence near the turbulent threshold for equivalent pipe flow. Under these conditions we can expect a treatment of convection mass transport using a well-mixed approximation to be reasonably accurate, as long as we take into account the initial transient phase during which the convection process is established.

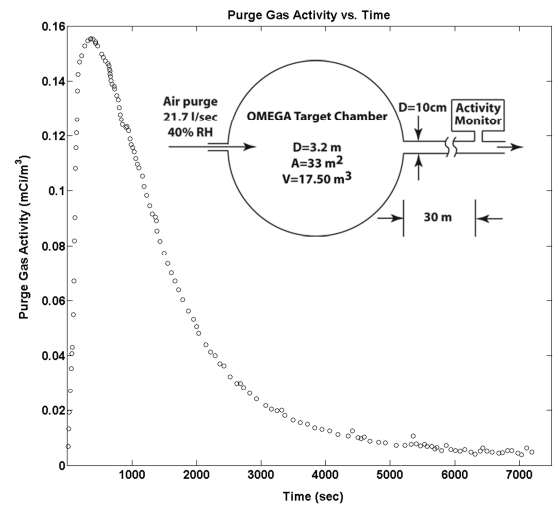


Fig.2 Omega chamber purge configuration and effluent versus time (After Ref.3).

#### IV. TIME SCALES OF RATE-LIMITING TRITIUM RELEASE PROCESSES

The fastest possible transport process between chamber and detector is bulk flow of gas-phase tritium from the process chamber to the detector. If gas-phase tritium (presumably HTO) is present in the chamber at the beginning of the purge, the signal in the detector would evolve as depicted by the model curve in Fig.3. It is evident therefore, that the observed tritium release rate is much slower than would be produced by bulk flow alone.

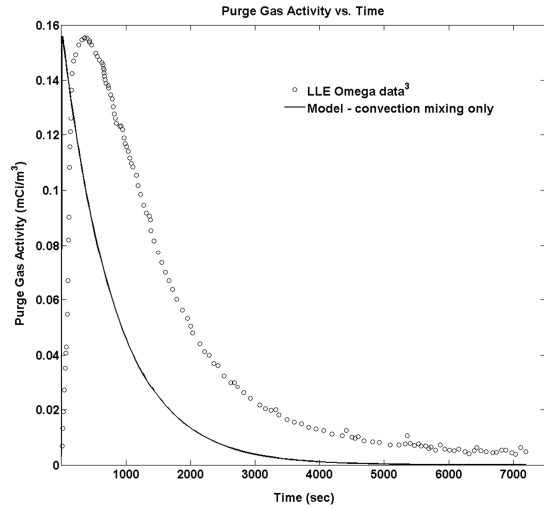


Fig.3 Calculated signal corresponding to bulk flow compared to the observed tritium signal.

When the purge data is examined using log-log scales (Fig.4) indications of multiple processes running over a range of characteristic time scales become apparent. The

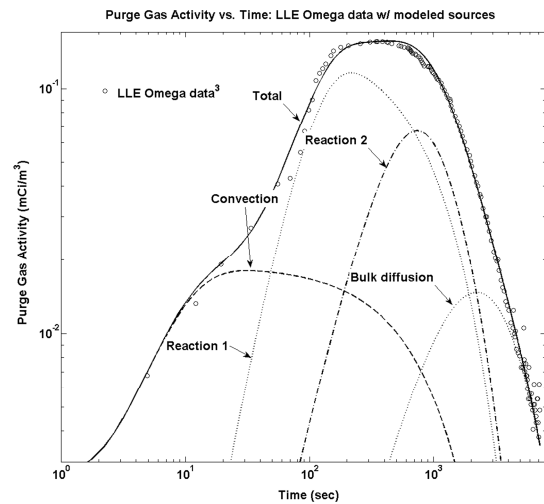


Fig.4 Multiple rate-limiting processes evident in the log-log plot of purge effluent concentration vs. time.

second fastest possible transport process involving the convection transport of loosely bound surface HTO into the gas phase will be limited by the convection mass transfer coefficient for the chamber. Because the mixing time-constant is approximately  $V_{ch}/Q_{purge} = 780 \text{ sec}$ , (13 min), which is significant on the time scale of the observed initial tritium release, we must estimate a time-dependent mass transfer coefficient in order to properly identify the convection mass transport time scale.

Using a CFD model of the chamber flow with fixed wall HTO concentration we find the transient mass transfer coefficient approximately follows a regular form so we use an exponential function fit to  $k'_G(t)$  obtained from the simulation in all subsequent transport calculations. We also use the CFD model to examine the appropriateness using a well-mixed approximation to describe the chamber convection and find the error compared with the predicted instantaneous local output concentration to be less than 5%.

Later peaks in tritium release are limited by rates of surface reactions between water supplied in the purge gas and surface-bound tritium, mainly associated with oxygen as -OT. Assuming the overall reaction mechanism of Eqn. 5, the minimum number of independent reactions able to describe the observed broad peak in tritium release according to Eqs.3-5 is two (Reaction 1 and Reaction 2 in Figs.4 and 5). The apparent contribution of diffusion from the bulk is dominant only at longer time scales and ultimately becomes the sole source of the persistent tail in the release curve (Fig.5).

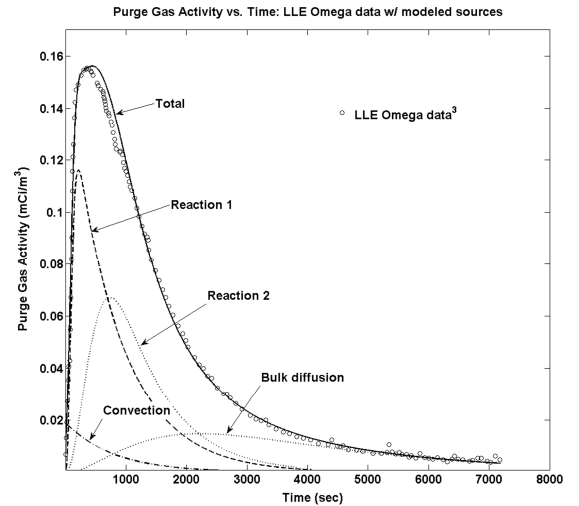


Fig.5 Measured and modeled tritium release from ICF chamber (linear scales).

#### V. DISCUSSION

Table I summarizes the initial conditions and constants found from the analysis and modeling of the

TABLE I. Best-fit parameters and constants

Parameters/ Constants	Value	Units
$\theta_{OT1_o}$	$1.5 \times 10^{-4}$	atom/site
$\theta_{OT2_o}$	$1.0 \times 10^{-4}$	atom/site
$\theta_{HTOp_o}$	$1.3 \times 10^{-5}$	atom/site
$s$	85	mol/m <sup>3</sup>
$D_{ab}/d_f$	$1.4 \times 10^{-11}$	m/sec
$k_{f1}$	$1.8 \times 10^{-4}$	(Pa-sec) <sup>-1</sup>
$k_{f2}$	$4.5 \times 10^{-5}$	(Pa-sec) <sup>-1</sup>
$k'_G$	$2.3 \times 10^{-4}$ - $4.2 \times 10^{-2}$	mol/m <sup>2</sup> -sec

chamber purge data. Assuming a total surface site density of  $1.0 \times 10^{19}$  (sites/m<sup>2</sup>) the total initial tritium surface concentration determined from the best-fit to the data is  $4.2 \times 10^{-9}$  mol/m<sup>2</sup>. This initial condition is consistent with the surface concentration of  $3 \times 10^{-9}$  mol/m<sup>2</sup> (90  $\mu$ Ci/m<sup>2</sup>) estimated for the high range of expected concentration based on chamber surface measurements following typical DT experiments on Omega<sup>3</sup>. The model also indicates the presence of a thin surface film of modest tritium solubility ( $s * \theta_{TOT_o} = 2.1 \times 10^{-2}$  (mol/m<sup>3</sup>)) on a tritium-insoluble base material. This finding is consistent with the fact that the chamber is primarily constructed of aluminum, a very low hydrogen solubility material which nearly always has a surface oxide film. Only the ratio of tritium diffusivity to film thickness can be obtained from the fit to the data, but if we assume a typical native oxide thickness of 10 nm, the corresponding diffusivity is  $1.4 \times 10^{-19}$  m<sup>2</sup>/sec, a value somewhat higher than has been reported ( $5 \times 10^{-24}$  m<sup>2</sup>/sec) for deuterium in crystalline  $\alpha$ -alumina monohydrate<sup>6</sup> but not necessarily unreasonable for a thin and potentially poorly ordered surface film in an ICF reactor.

Exact attribution of the model reaction rates to specific materials or surface species is not strictly possible owing to the composite nature of the Omega target chamber. One interpretation however is that because the process chamber is composed mainly of aluminum and silica optical windows, each observed reaction corresponds to a particular material. Alternately, tritium hold up could be dominated by one material or the other, and the two reaction rates could be characteristic of differing but discrete bonding states of tritium on a single surface type. Still another interpretation is that the two modeled rates actually represent an approximation to a continuous range of rates corresponding to a range of tritium bonding states on one or both materials. All these views are in principle complimentary and non-exclusive. Consequently, the identification here of two dominant reactions only represents a minimal specification necessary to plausibly explain the data and we must await the results of individual testing of constituent materials currently under way to understand the reaction rates in isolation.

The quantitative role of water can also only be approximately assessed from the analysis of this single data set. As written, the model reaction Eq.(4) predicts linear rate dependence on water partial pressure, however at constant humidity, the analysis cannot test this hypothesis and water concentration (whether in the gas or adsorbed phase) becomes implicitly lumped into the net reaction rate constants. The mechanism of Eq.(5) is therefore the simplest one consistent with the data, though not necessarily the only one. Through systematic variation of relative humidity however, it should be possible to pinpoint precise reaction mechanisms and, to the extent adsorbed water plays a direct role in rate-limiting reactions (as opposed to gas-phase water partial pressure), the functional form of the adsorption equilibrium relation for water on these surfaces should be obtainable as well.

## VI. CONCLUSION

A generalized system-level model has been proposed to explain the observed tritium release characteristics of an ICF chamber during exposure to a constant flow of humid air. The strength of the approach lies in the direct connection of observable purge stream tritium concentration to the underlying rate processes through a complete system of mass balances extending down to the bulk absorption level through surface phenomena involving simultaneous reaction and transport between phases.

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